THE BEHAVIOR OF THE NATURAL RADIONUCLIDES IN WESTERN COAL-FIRED POWER PLANTS

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The projected dependence of the nation on coal-produced electrical energy necessitates a thorough study of the associated environmental risks. One potential hazard worthy of further investigation is the release of natural radionuclides upon coal combustion. Radioactive effluents from both fossil-fuel and nuclear power plants have been compared.[1,2] However, oversimplifications and lack of good emission data for radionuclides from the fossil-fuel plants lead to differing conclusions. Hull[3] has compared the inorganic-effluent releases of the fossil-fuel plants to the radionuclide releases from nuclear plants in terms of accepted environmental standards for each type of effluent. Moore et al.[4] have calculated that anthropogenic sources contribute 6.5% of the total ^{210}Po atmospheric flux for the continental U.S. Fossil-fuel burning makes up 14% of these anthropogenic sources or 1% of the total ^{210}Po input. One can determine a maximum concentration indirectly from the ^{210}Pb content in the coal, since ^{210}Pb is the grandparent of ^{210}Po in the ^{238}U-decay series. None of the fossil-fuel-plant studies have concentrated on the radionuclide-combustion chemistry, which is necessary to make valid comparisons between fossil-fuel and nuclear plants. It is the purpose this work to study the chemical fractionation of the natural radionuclides in coal during combustion.

Experimental

Coal, bottom-ash, and electrostatic precipitator (ESP) fly-ash samples were obtained from two western coal-fired power plants. Plant A burns low-sulfur (0.52%), low-ash (9.2%) coal and Plant B burns low-sulfur (0.46%), high-ash (23.2%) coal. We also obtained from Plant B kilogram quantities of particle-sized stack fly ash. This stack fly ash was collected by a large cyclone separator mounted at the outlet of one of the ESP units.[5] Two separate sets of the four sized fractions were obtained. For each fraction as determined by centrifugal sedimentation, the mass median diameters (mmd) were 17, 6, 3.8, and 2.5 μm, Geometric standard deviations of the fractions were approximately 2.3, 2.1, 1.7, and 1.8 μm, respectively.

All samples were ground to 200 mesh when necessary, homogenized, packaged, and then counted for natural gamma radiation on an ultra-low background, Compton-suppression, gamma-ray spectrometer.

The ^{238}U natural radioactive-decay-chain series was found to be in secular equilbrium in the coal samples but not in the ash samples. During the combustion process a potential exists for decay-chain disequilibrium to occur, since many of the daughter radionuclides have quite different chemical and physical characteristics. Secondary post-fractionation radionuclides are those whose half-lives are long enough to produce gamma rays or gamma-ray-emitting daughters after secular equilibrium has been disrupted by the combustion process. The actual measured gamma ray may originate from a daughter further along the decay chain but prior to the next long-lived species.

The half-lives of these intermediary radionuclides are short enough so that secular equilibration can be assumed to have been reestablished for that section of the decay chain. The packaged samples were allowed to sit for 6 months. This provided the longest-lived intermediary radionuclide ^{234}Th (24.1 day) the opportunity to come to within 1% of secular equilibration with its parent ^{238}U.

Discussion

Enrichment factors relative to the input coal were calculated for the radionuclide contents observed. The enrichment factor (EF) is defined as the ratio of the concentration of a radionuclide (X) and ^{40}K in the sample, divided by the corresponding ration in the input coal.

$$EF = \frac{[X] \text{ sample}/[^{40}K] \text{ sample}}{[X] \text{ coal}/[^{40}K] \text{ coal}}$$

This effectively normalizes the apparent enrichment resulting from loss of carbon during the combustion process. Potassium-40 is used in this normalization calculation because its concentration remains constant in all samples; hence it was assumed to be a tracer for the alumino-silicate-dominated ash matrix.

Table 1 presents the EF value for the different samples from both plants. The ESP fly ash and bottom ash from both plants show no enrichment of the ^{232}Th-decay-chain daughters. This is expected since thorium and radium are essentially refractory elements and should remain with the ^{40}K in the ash matrix. Uranium behaves in quite

Table 1. Enrichment factor relative to input coal and normalized to ^{40}K[a]

Decay-chain origin	^{232}Th		^{238}U			^{235}U
Source after fractionation	^{228}Th	^{228}Ra	^{210}Pb	^{226}Ra	^{238}U	^{235}U
Plant A[b]						
ESP fly ash	0.89	0.90	0.48	1.02	0.71	0.70
Bottom ash	0.96	0.97	0.24	0.99	0.70	0.64
Plant B[c]						
ESP fly ash	0.96	0.98	0.74	1.02	0.94	0.85
Bottom ash	0.91	0.89	0.29	0.90	0.76	0.73
Scrubber ash	1.01	1.03	0.95	1.08	0.97	0.88

[a] $\pm$10 to 20% propagated 1σ error from the mean.

[b] Samples from Plant A; input coal contains 11.3% H_2O, 9.2% ash, and 0.52% sulfur.

[c] Samples from Plant B; input coal contains 6.8% H_2O, 23.2% ash, and 0.46% sulfur.

a different manner. Both ^{235}U and ^{238}U show significant depletion in the fly ash from Plant A (low-ash coal) and the bottom ash from both Plants. The fly ash is not nearly as depleted in these uranium isotopes from Plant B (high-ash coal).

Lead-210 appears to be the most volatile radionuclide measured. It is quite depleted in the bottom ash from both plants and is less depleted in the fly ash from Plant B (high-ash coal). All EF values for the scrubber ash are close to unity. The wet scrubber is more efficient than the ESP for fly-ash removal (99.2% vs 97.%) and, therefore, retains more ash by weight than the ESP unit although it releases higher numbers of submicron particles to the atmosphere.[6] Since the wet scrubber is more efficient, its EF value might be expected to be near unity, and consequently any chemical enrichment in the submicron particulates would be obscured.

The ^{210}Pb depletion in the ESP bottom ash probably occurs as volatilization and later condensation onto the fly-ash matrix. Since heterogeneous condensation is a surface-area phenomenon, the lead would be expected to be enriched on the finer fly-ash particles. In Fig. 1, the stack (post ESP) sized fly ash shows a very strong increase in EF with decreasing particle size. This effect is consistent with the depletion of lead on the larger-sized ESP fly ash. Davison et al.[7] discuss this condensation mechanism more fully.

Assuming that secular equilibration exists between ^{210}Pb and [210]Po in the coal samples, the specific activity for both nuclides will be identical and therefore the total inventory of [210]Po for the coal combustion system can be estimated. Its post-combustion behavior was not studied in this work; but since polonium is more volatile than lead, it will probably condense onto the extremely small fly-ash particles after combustion. A study of the combustion chemistry and deposition properties of this important radionuclide is in progress.

Uranium's definite association with small particles has been previously observed.[8,9] It is slightly depleted in the bottom ash of both plants. Plant B (high-ash coal) has a fly-ash EF close to unity. However, this plant's sized stack fly ash shows a very definite EF increase with decreasing particle size (see Fig. 1). We propose a bimodal mechanism to explain this behavior. The coal contains uranium in two different phases, which affects its volatility upon combustion. Klein et al.[9] observed that uranium behaves in a manner intermediate between those elements remaining with the slag and those elements concentrating on the fly ash.

Breger[10] suggests that uranium enters the coal bed from ground water as the soluble uranyl dicarbonate $Na_2[UO_2(CO_3)_2]$ or sodium uranyl tricarbonate $Na_4[UO_2(CO_3)_3]$ complex. The slightly acidic environment of the coal decomposes this complex and the uranium quickly becomes absorbed by the coal with subsequent reduction to uraninite UO_2. If sufficient silica is present in solution, the mineral coffinite $U(SiO_4)_{1-x}$ $(OH)_{4x}$ can form instead of uraninite. Since the uranium is in solution, it can migrate from cracks and joints into the coal matrix for some distance and can, therefore, be expected to reside in the coal in a very highly dispersed state. Uranium is enriched over thorium in these samples (Th/U = 2.0) compared to the average crustal ratio (Th/U = 4.0),[11] thus indicating the high mobility of uranium as compared to thorium during ground and surface water transport.

The characteristics of uranium during the combustion process depend upon the conditions of the furnace as well as its chemical and physical form in the input coal. Coal-fired power plants operate their burners with about a 10% stoichiometric excess of oxygen.[12] This should result in an oxidizing combustion environment with a temperature range of 1500 to 1600°C. Under these conditions, the volatile species UO_3 could be expected to form.[13,14] The possibility also exists for uranium to become incorporated into a silica melt during combustion if it were originally associated with a silicate (i.e., coffinite).

The existence of uranium bimodally in the coal can therefore give rise to both a volatile and nonvolatile species simultaneously, since both uraninite and coffinite can coexist in the pulverized and semihomogenized coal. The data in Table 1 support this relationship. The Plant B (high-ash coal) fly ash shows less uranium depletion than the Plant A (low-ash coal) fly ash. A higher percentage of the uranium is probably associated with the alumino-silicate minerals and is consequently available for incorporation into the silica-rich fly-ash matrix.

Thorium-228 could be slightly enriched in the stack fly ash when compared to INAA (Instrumental Neutron Activation Analysis) data for cerium, a nonenriched element

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(see Fig. 1). Thorium (and to some extent uranium) is normally associated with the very chemically resistant mineral zircon $ZrSiO_4$,[15] which is a ubiquitous accessory mineral in many common rocks. Zircon does not weather easily and is commonly found in sedimentary environments. It is conceivable that the thorium observed in the coal system was deposited contemporaneously with the coal along with the other silicate-based minerals. These minerals make up the ash after the coal is burned. The small resistant mineral grains could be carried with the gases after combustion and follow the course of the fly ash. The thorium behavior in the sized fly ash could be explained if thorium existed in the coal as submicron particles.

The enrichment of ^{228}Ra and ^{226}Ra (see Fig. 1) is difficult to explain. Klein et al.[9] observes that barium (and hence probably radium) and thorium become incorporated into the fly-ash matrix. However, barium is known to form a volatile species $Ba(OH)_2$ in the presence of steam, and radium may also form a corresponding species. Figure 1 shows ^{226}Ra with a greater EF than ^{228}Ra. A portion of the ^{226}Ra will reside with the uraninite fraction of its ^{238}U parent as described earlier. This probably allows ^{226}Ra to form a more mobile species than the silicate bound ^{228}Ra (from the ^{232}Th chain) in a manner similar to the bimodally located uranium.

The behavior of the natural radioactive decay series throughout the coal deposition, combustion, and emission system can be described by the following:

● Associated with the accumulation of orgainic matter is a significant fraction of clay minerals, sand, and other inorganic sedimentary material. These materials contain the alumino-silicate minerals that will later comprise the coal fly ash and bottom ash. Herein is found the source of the ^{232}Th, ^{40}K, and a part of the silicate associated uranium.

● The organic accumulation environment ceases and a deposition environment prevails, which buries the organic matter. Coal metamorphism occurs.

● Ground and surface waters penetrate down through the overburden, invading the coal. These waters contain uranium as soluble uranyl carbonate salts and varying amounts of soluble silica.

● Uranium is absorbed by the coal and reduced to uraninite or coffinite, depending on the silica content of the water.

● Coal is mined, pulverized, and fed into the furnace for power production. Much of the alumino-silica minerals (mostly clay) form a melt and drop out as slag. Most of the thorium and radium isotopes follow. Lead-210 remains volatile and continues along with the gases and fly ash to the emission control system. Much of the uranium that is associated with the clays, or that which was mineralized as coffinite, also remain with the bottom ash. The uranium that is dispersed in the coal as uraninite becomes volatile as the UO_3 species and continues along with the gases, lead, and the fly ash.

● Somewhere down the flue line, first uranium and then lead preferentially condense out on the finer fly-ash particles because they have a high surface to mass ratio.

● The ESP collects most of the particulate mass. Those finer particles that bypass the ESP continue up the stack with the gases. They are very enriched in ^{210}Pb relative to the coal, and moderately enriched in ^{235}U and ^{238}U. Some slight enrichment is observed for ^{226}Ra (probably that associated with uraninite), ^{228}Ra, and ^{228}Th. The thorium is probably associated with fine zircon grains.

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The degree to which each of the many possible mechanisms affect the final radio-nuclide concentrations cannot be ascertained from these data. The actual situation may be one mechanism, or more probably a combination of mechanisms. The mineralogical or chemical form in which the radionuclides or trace elements exist in the coal does have an important effect on their subsequent combustion chemistry and emission characteristics.

References

1. Eisenbud, Merril and Henry G. Petrow, Science 144, 228 (1964).
2. Martin, J.E., Harward, E.D., Oakley, D.T., Smith, J.M., and Bedrosian, P.H., in IAEA Symposium on Environmental Aspects of Nuclear Power Stations, New York, IAEA Conf. 700810-24 (1969) paper - IAEA-Sm-146/19, 325-337.
3. Hull, A.P., Nuclear News, 51-55, (April, 1974).
4. Moore, H.E., Martell, E.A., and Poet, S.E., Environ. Sci. Technol. 10, 586, (1976).
5. McFarland, A.R., Fisher, G.L., Prentice, B.A., and Bertch, R.W., Submitted for publication in Environ. Sci. Technol. (1976).
6. Ondov, J.M., Ragaini, R.C., and Biermann, A.H., presented at Amer. Chem. Soc. Meeting, Div. of Environ. Chem., Preprint UCRL-78050, 1976.
7. Davison, R.L., Natusch, D.F.S., and Wallace, J.R., Environ. Sci. Technol. 8, 1107 (1974).
8. Ragaini, R.C., Ondov, J.M., Proc. Int. Conf. Modern Trends in Activation Analysis, Munich, 1976, I, 654; Lawrence Livermore Laboratory, Preprint UCRL-77669.
9. Klein, D.H., Andren, A.W., Carter, J.A., Emery, J.F., Feldman, C., Fulkerson, W., Lyon, W.S., Ogle, J.C., Talmi, Y., Van Hook, R.I., and Bolton, N., Environ. Sci. Technol. 9, 973 (1975).
10. Breger, I.A., in IAEA Symposium on the Formation of Uranium Ore Deposits, Athens, IAEA-SM-183/29 (1974) pp. 99-124.
11. Mason, B., Principles of Geochemistry, 3rd. Ed., John Wiley & Sons (1966).
12. Babcock and Wilcox, Steam, Its Generation and Use, 38th Ed., Babcock and Wilcox, New York, 1972.
13. Rand, M.H., and Kubaschewski, O., The Thermochemical Properties of Uranium Compounds, Interscience (Wiley), New York, 1963.
14. Ackermann, R.J., Thorn, R.J., Alexander, C., and Tetenbaum, M., J. Phys. Chem. 64, 350 (1960).
15. Kirby, H.U., Mound Laboratory, Rept. MLM-2111 (1974).

Enrichment factors of ^{210}Pb, ^{238}U, ^{226}Ra, ^{228}Ra and ^{228}Th vs. size in the stack fly ash collected downstream from an ESP. The cerium concentrations are taken from INAA analysis of the same samples.

$$EF = \frac{[X]\ FLY\ ASH/[^{40}K]\ FLY\ ASH}{[X]\ COAL/[^{40}K]\ COAL}$$

Enrichment factor

5.0

4.0

3.0

2.0

1.0

γ-COUNTING DATA:

○ ^{210}Pb

△ ^{238}U

▽ ^{226}Ra

▣ ^{228}Ra

◇ ^{228}Th

INAA data:

● Ce

0   5   10   15   20

Particle size, μ